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(54) Method for the Preparation of
Well Servicing Fluids

(57) A method for preparing a well
servicing fluid containing a hydrophilic
polymer in which the hydrophilic
polymer and water are admixed to

form a uniform polymer/water
suspension followed by the
dissolution of a dry inorganic salt
having a positive heat of solution, the
amount of salt added being such as to
raise the temperature of the
polymer/water suspension to above
about 70°C.

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SPECIFICATION

Method for the Preparation of Well Servicing Fluids

The present invention relates to the preparation of polymer containing brines useful in various applications wherein an increase in viscosity, filtrate control or other functional property is derived from the polymer composition contained therein.

Polymer containing brines are useful as well servicing fluids such as drilling fluids, workover fluids, completion fluids, packer fluids, well treating fluids, subterranean formation treating fluids, spacer fluids and hole abandonment fluids and in other applications wherein thickened aqueous mediums are required. It is known to use hydrophilic polymers such as hydroxyethyl cellulose (HEC), for example, as thickening agents for aqueous mediums such as those used in well servicing fluids. However, such polymers are not readily hydrated, solvated or dispersed in aqueous solutions containing one or more water soluble salts of multivalent cations such as the heavy oil field brines having a density greater than about 1.39 g per ml preferred for the preparation of well servicing fluids. Elevated temperatures and/or mixing under high shear for extended periods of time are required for effective thickening of such brines with hydrophilic polymeric materials in order to obtain a homogeneous mixture. In many cases, as, for example, in workover operations, the equipment available for preparing the well servicing fluids does not really lend itself to such conditions. Accordingly, it is usually necessary, if it is desired to use such thickened brines, to prepare them off the well site or to circulate the fluid in the hot borehole.

It is, therefore, an object of the present invention to provide a method for the preparation of thickened polymer containing brines, especially heavy brines having a density greater than 1.39 g per ml under conditions of low shear mixing without the application of heat.

Other objects and advantages of the invention will become apparent from the following description thereof, together with the appended claims.

According to the invention, a suspension of a hydrophilic polymer and water is formed by generally uniformly dispersing the polymer in the water. An inorganic salt having a positive heat of solution is then added to the suspension, in the absence of external heating, the amount of salt added being sufficient to raise the temperature of the dispersion to above 70° as a result of the heat of solution of the salt. This suspension, depending on the density desired, can be used directly as a well servicing fluid.

In another embodiment of the invention, there is added to the liquid suspension of the polymer, a sufficient quantity of a heavy aqueous brine to provide a quantity of a well servicing fluid of the desired density.

The hydrophilic polymers useful in the practice of the invention are particulate organic polymers which are generally water soluble or water dispersible and which upon solution or dispersion in an aqueous medium increase the viscosity of the system but which do not readily hydrate, solubilize or disperse upon addition to heavy brines having a density greater than 1.39 g per ml and containing soluble salts of multivalent cations. Such polymers are selected from the group consisting of cellulose derivatives, water dispersible starch derivatives, polysaccharide gums, and mixtures thereof. Exemplary cellulose derivatives are the carboxyalkyl cellulose ethers, such as carboxymethyl cellulose and carboxyethyl cellulose; hydroxyalkyl cellulose ethers such as hydroxyethyl cellulose and hydroxypropyl cellulose; and mixed cellulose ethers such as: carboxyalkyl hydroxyalkyl cellulose, i.e. carboxymethyl hydroxyethyl cellulose; alkyl hydroxyalkyl cellulose; i.e. methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose; alkyl carboxyalkyl cellulose, i.e. ethyl carboxymethyl cellulose. See U.S. Patent No. 4,110,230. Exemplary starch derivatives are the carboxyalkyl starch ethers such as carboxymethyl starch and carboxyethyl starch; hydroxyalkyl starch ethers, such as hydroxyethyl starch and hydroxypropyl starch; and mixed starch ethers such as: carboxyalkyl hydroxyalkyl starch, i.e. carboxymethyl hydroxyethyl starch; alkyl hydroxyalkyl starch, i.e. methyl hydroxyethyl starch; alkyl carboxyalkyl starch, i.e. ethylcarboxymethyl starch. Exemplary polysaccharide gums include: the biopolymers such as Xanthomonas (xanthan) gum; galactomannan gums, such as guar gum, locust bean gum, tara gum; glucomannan gums, and derivatives thereof, particularly the hydroxyalkyl derivatives. See U.S. Patents Nos. 4,021,355 and 4,105,561.

Other polymers which can be used include pre-gelatinized starch powder and stabilized partially dextrinized polysaccharide powder, toxic nonionic.

Particularly preferred are the HEC polymers which are generally high yield, water soluble, non-ionic materials produced by treating cellulose with sodium hydroxide followed by reaction with ethylene oxide. Each anhydroglucose unit in the cellulose molecule has three reactive hydroxy groups. The average number of moles of the ethylene oxide that becomes attached to each anhydroglucose unit in cellulose is called moles of substituent combined. In general, the greater the degree of substitution, the greater the water solubility. In general, it is preferred to use HEC polymers having as high a mole substitution as possible.

Usually, upon the addition of one of the dry particulate hydrophilic polymers described above to aqueous mediums such as brines, the polymer particles undergo surface hydration preventing the interior of the particle from readily hydrating, solvating or otherwise dispersing in the aqueous medium.

Accordingly, high shear, long mixing times and/or elevated temperatures must be applied in order to obtain a homogeneous system. Using the method of the present invention, the hydrophilic polymers readily hydrate, dissolve or disperse in the aqueous brine at relatively low shear and ambient temperatures.

5 In the initial step of the method, the hydrophilic polymer and water as, for example, fresh water, distilled water, etc., are admixed under conditions so as to provide a uniform dispersion of the polymer in the water. The term "uniform dispersion" as used herein refers to a condition in which the polymer and water form a generally homogeneous system whether it be a solution or a mixture in which discrete polymer particles are generally uniformly distributed through the suspension of polymer and water. The polymer and water can be admixed by conventional mixing techniques and no special conditions of temperature, mixing times or other such parameters are required. It is only sufficient that the polymer and water be admixed sufficiently to provide the uniform dispersion of the polymer suspension in the water. 10

15 In the next step of the method, an inorganic salt(s) is added, in dry form, to the suspension of the polymer and water, the salt being of a type which has a positive heat of solution and brine generates heat upon dissolving in water. The amount of the inorganic salt added to the polymer suspension will be such as to provide a temperature of above 70°C as a result of the heat of solution of the salt and without the addition of external heating. Dissolving of the salt in the polymer suspension can be conducted with usual mixing techniques. 15

20 The inorganic salt or salts which can be employed in the second step of the method are any water soluble salts which generate heat upon dissolving in water and which preferably form brines which are useful in hydrocarbon recovery operations. Preferred salts are those selected from the group consisting of calcium chloride, calcium bromide, zinc chloride, zinc bromide, and mixtures thereof. As noted, preferably the amount of salt added should be such as to raise the temperature of the polymer/water suspension to above about 70°C. However, it is preferred that the amount of salt added be such as to raise the temperature to at least 80°C and most preferably to at least 90°. It will be apparent that different salts have different positive heats of solution and, therefore, the amount of salt or salts added will be dependent upon the particular salt(s) which are selected. 20 25

30 The polymer/water suspensions prepared as above can themselves be used as well servicing fluids if the amount of inorganic salts added are sufficient to achieve the desired density. Thus, for example, in a typical case, the amount of polymer, water and inorganic salt admixed may be sufficient to form a thickened brine of the desired density. More frequently, however, there is added to the polymer/water suspension containing the dissolved salt an aqueous brine solution of a given density, the aqueous brine being added in an amount so as to provide a well servicing fluid having a predetermined density. In this latter embodiment of the method of the present invention, the polymer, water and inorganic salt are mixed as above to hydrate the polymer and form the polymer/water suspension. Following this, the aqueous brine is admixed with the polymer/water suspension containing the inorganic salt and the well servicing fluid thus prepared. The aqueous brines which can be admixed with the polymer/water suspensions generally contain soluble salts such as, for example, a soluble salt of an alkali metal, an alkaline earth metal, a Group Ib metal, a Group IIb metal as well as water soluble salts of ammonia and other cations. Generally speaking, such aqueous brines contain soluble salts of multivalent cations, e.g. Zn and Ca. Thus, aqueous brines comprised of a salt selected from the group consisting of calcium chloride, calcium bromide, zinc chloride, zinc bromide, and mixtures thereof are especially preferred. The aqueous brines will generally have densities ranging from 1.39 to 2.30 g per ml. 30 35 40 45

45 The amount of the hydrophilic polymer used in the method of the present invention will be such as to provide a final concentration of from 0.25 to 30 g per litre regardless of whether the ultimate well servicing fluid comprises (a) the polymer/water suspension prepared by mixing the polymer, water and the inorganic salt, or (b) the polymer, water, inorganic salt and an amount of an aqueous brine.

50 While the mechanism of the method of the present invention is not completely understood, it has been found that brine solutions produced thereby have improved rheological and filtration properties as opposed to brine solutions prepared simply by dispersing the hydrophilic polymer, in dry form, in a brine and then heating the mixture to solvate the polymer. The application of artificial heat to the mixture of a hydrophilic polymer and a brine while giving some enhanced results, does not achieve the remarkable results obtained by the method wherein the polymer is first dispersed in water and this suspension then brought to elevated temperature via the mechanism of the natural heat of solution of the inorganic salt(s) dissolving in the polymer/water suspension. To more fully illustrate the present invention, the following non-limiting examples are presented. Unless otherwise indicated, all physical property measurements were made in accordance with testing procedures set forth in Standard Procedure for Testing Drilling Fluid, API RP 13B, Seventh Edition, April, 1978. In the following examples, the following hydrophilic polymers were employed: 50 55 60

65 Hi Vis Cellex (carboxymethyl cellulose)
Barazan (zanthan gum)
Natrashol 250 HHR (hydroxyethyl cellulose)
Drispac (polyanionic cellulose powder)

Bohramyl (cross-linked hydroxyethyl starch)
 Impermex (pregelatinized starch powder)
 Dextrid (stabilized partially dextrinized polysaccharide powder, toxic, non-ionic).

Example 1

- 5 Several hydrophilic polymers were used to prepare thickened aqueous brines as described below. 5
 Approximately 2 g of the polymer was mixed in 204.4 g of water by means of a Multimixer for about
 10 minutes. Thereafter, there was added to the prehydrated polymer 114.0 g of CaCl_2 pellets (94—
 97%) and 280.5 g of CaBr_2 (91%) followed by 16.8 ml of a 19.2 ppg $\text{CaBr}_2/\text{ZnBr}_2$ brine to bring the
 10 density of the resulting brine to 1.82 g/ml. The heat of solution of the added salts brought each sample
 to boiling (100°C). The resulting thickened mixtures were allowed to stand overnight at ambient
 10 temperature and the rheological and filtration properties of each mixture were then determined.
 Rheological properties were measured using a Fann Model 35A Viscometer and a Brookfield RVT
 Viscometer. The filtration properties were measured on an API filtration press. The properties reported
 are plastic viscosity (PV) cp, Yield Point (YP) Kg/m² apparent viscosity (AV) cp, 10-second gel strength
 15 (GEL 10 s) Kg/m², and API filtrate (API-FIL) ml. All filtration testing was performed after 28.5 g/l CaCO_3 15
 was added as a bridging agent. Results of the measurements made are presented in Table 1 below.
 Table 2 gives the same information for identical samples after being rolled for 16 hours at 65.5°C.

Table 1

		PV	YP	AV	GEL 10s	API FIL	
20							20
	Cellex HV	—	0	150+	1.196	1.5	
	Barazan	92	1.465	109	0.122	6.5	
	Drispac	—	—	150+	2.002	0.5	
	Bohramyl	80	0.195	82	0.098	3.0	
25	Impermex	72	0.293	74	0.098	100	25
	Dextrid	73	0.293	76	0.073	53	

Table 2

		PV	YP	AV	GEL 10 s	API FIL	
30							30
	Cellex HV	—	—	150+	0.537	0.5	
	Barazan	—	—	150+	0.293	4.5	
	Drispac	—	—	150+	0.439	0.5	
	Bohramyl	76	0.195	78	0.098	1.0	
	Impermex	62	0.195	64	0.098	77	
35	Dextrid	68	0.293	71	0.098	89	35

Example 2

- Control thickened aqueous brine solutions were prepared by adding 2 g of each of the dry
 polymers employed in Example 1 to a pre-made 1.82 g/ml brine prepared by mixing 214.2 g of H_2O ,
 119.5 g of CaCl_2 , 294.0 g of CaBr_2 and 16.2 ml of a 2.30 g/ml $\text{CaBr}_2/\text{ZnBr}_2$ brine. Data on the
 40 rheological and filtration properties of the control samples after standing overnight are presented in
 Table 3 below while similar data on identical samples after being rolled for 16 hours at 65.5°C are
 presented in Table 4 below. These data compared to those in Tables 1 and 2 demonstrate that the
 brines prepared by the method of the invention (Example 1) wherein the polymer is first hydrated and
 the dry salts added thereto exhibit superior viscosity and give lower filtrates in every case before hot
 45 rolling and in substantially all cases after hot rolling. 45

Table 3

		PV	YP	AV	GEL 10 s	API FIL	
50							50
	Cellex HV	54	0	54	0.098	180	
	Barazan	46	0	46	0.073	201	
	Drispac	55	0.049	55	0.073	174	
	Bohramyl	49	0.049	49	0.049	190	
	Impermex	51	0.049	52	0.098	172	
	Dextrid	51	0.049	51	0.073	170	

Table 4

		PV	Y%	AV	GEL 10 s	API FIL
5	Cellex HV	49	0	50	0.098	250
	Barazan	67	—	67	0.073	1
	Drispac	50	0.146	52	0.073	262
	Bohramyl	73	—	71	0.073	6
	Impermex	67	0.293	70	0.098	42
	Dextrid	65	—	64	0.073	6

10 Example 3

Using the method described in Example 1, polymer containing aqueous brines of several different densities were prepared. Five grams of Hi Vis Cellex were prehydrated in water by mixing for 10 minutes. Dry CaCl_2 pellets were added to the prehydrated polymer with mixing to obtain a Hi Vis Cellex concentrate of 1.39 g/ml density. One hundred forty ml of the concentrate was added to 210 ml of an aqueous brine of 1.39 g/ml density to achieve a polymer concentration. In the same manner, heavy aqueous brines of density 1.70 and 2.04 g/ml were prepared. The composition of each of the aqueous brines is listed in Table 5 below.

Table 5

		Density (g/ml)		
		1.39	1.70	2.04
20	Water, ml	299.6	234.2	112.2
	CaCl_2 , g	197.7	137.9	62.6
	CaBr_2 , g	—	224.3	154.1
25	(Density 2.30 g/ml) brine (ml)	—	—	166.6

Control samples of thickened aqueous brines were prepared by mixing 2 g of the dry Hi Vis Cellex with premade brines having densities of 1.39, 1.70 and 2.04 g/ml respectively. Rheological and filtration measurements of the samples prepared by the method of Example 1 and the control samples were made as described in the foregoing examples. Results are presented in Table 6. In Table 7, the data obtained on all the samples after hot rolling at 65.5°C for 16 hours are presented. It is obvious from these data that the apparent viscosities of the brines prepared by the method of the invention have values twice as large or more than the controls. The superior filtration properties of the samples prepared by the method of the invention are readily evident as well from a comparison of these data.

Table 6

		1.39 g/ml		1.70 g/ml		2.04 g/ml	
		Ex. 1 Prep	Control	Ex. 1 Prep	Control	Ex. 1 Prep	Control
35	PV	14	7	35	6	29	20
	YP	0.098	0.049	—	0.049	0.830	0
	AV	15	8	34	7	38	20
	40 GEL 10 s	0.073	0.049	0.098	0.049	0.146	0.049
	API-FIL	12	330	0.5	330	0.5	330

Table 7

		1.39 g/ml		1.70 g/ml		2.04 g/ml	
		Ex. 1 Prep	Control	Ex. 1 Prep	Control	Ex. 1 Prep	Control
45	PV	21	9	38	6	45	21
	YP	—	0	0.098	0.049	0.049	0.098
	AV	19	9	39	7	50	22
	GEL 10 s	0.195	0.024	0.195	0.024	0.195	0.024
	API-FIL	10	150	3	310	4	310

Example 4

Brines having a density of 1.85 g/ml and containing 1 ppb carboxymethyl cellulose, either Hi Vis Cellex (high Viscosity Grade) or Drispac, were prepared by adding the polymer to 176 ml (equivalent to 0.5036 bbl) water and mixing to dissolve the polymer. Thereafter, there were added, while mixing, 114 g CaCl_2 (95%) and 180 g CaBr_2 (91%) (equivalent to 114 and 280 ppb, respectively). The heat of solution of these salts increased the temperature to 100°C. The API rheology and fluid loss was determined on these viscous solutions after cooling to room temperature. The data obtained are given in Table 8.

Table 8

Polymer	600 rpm	300 rpm	AV	PV	YP	Gel Strength		API Fluid Loss ml
						10 Sec.	10 Min.	
Cellex	249	151	124	98	2.587	0.220	0.293	0
Drispac	223	136	111	87	2.392	0.195	0.244	0.1

Example 5

Various density brines containing 1.5 ppb hydroxyethyl cellulose (Natrolsol 250 HHR) were prepared by mixing the polymer with the amount of water indicated in Table 2. As the polymer hydrated in the water, the viscosity increased. Thereafter, the indicated amount of CaCl_2 (95% active) was added while mixing. The heat of solution of the CaCl_2 increased the temperature about 82°C and the solution became more viscous. The indicated amount of a 1.70 g/ml CaBr_2 solution was slowly added followed by the indicated amount of a 2.30 g/ml $\text{ZnBr}_2/\text{CaBr}_2$ solution. After cooling to room temperature in one hour, the API rheology and fluid loss were obtained. The solutions were then rolled at 65.5°C for 16 hours, cooled to room temperature, and the API rheology and fluid loss determined. The data are given in Table 9.

Example 6

Three Hi Vis Cellex polymer concentrates were prepared by dispersing 2 grams of the polymer in 3.89 ml of water. One concentrate (Control Sample) was diluted with 155.5 ml of H₂O followed by the addition of 114.0 grams of CaCl₂, 280.5 grams of CaBr₂ and 16.8 ml of 2.30 g/ml CaBr₂/ZnBr₂ brine.

5 The temperature of this sample reached 100°C.

A second concentrate (Sample A) was added to a brine solution at room temperature. The brine was prepared with 155.5 ml of H₂O, 114.0 grams of CaCl₂, 280.5 grams of CaBr₂, and 16.8 ml of 2.30 g/ml CaBr₂/ZnBr₂ brine. The mixing in of the concentrate caused heat evolution, bringing the sample temperature to 45.5°C. It was noted that insoluble clumps of carboxymethyl cellulose formed immediately. When cooled overnight, a large amount of suspended strings were formed which eventually floated to the surface. It did not appear that any of the polymer concentrate went into the brine solution.

10 A third concentrate (Sample B) was prepared as in the case of Sample A and once again heat was evolved when the concentrate was mixed in, the temperature reaching 44°C. Following this, Sample B was rolled at 100°C for 3 hours in an aging cell. Sample temperature was measured at 71°C after aging. Although some suspended strings of polymer formed and floated to the top, most of the polymeric concentrate appears to have been dispersed.

15 The above three samples were then rolled for 64 hours at 65.5°C. Following cooling, they were run on a Brookfield Viscometer at 50 rpm. The Control Sample maintained a reading of 1590 cp and exhibited a smooth consistency, as before rolling.

20 Most of the insoluble clumps and all of the suspended strings dissolved in Sample A. The Brookfield reading was, nevertheless, only 180 cp.

Sample B, which appeared homogeneous, showed a Brookfield reading of 250 cp.

25 From the above results, it can be seen that simply prehydrating the polymer in water alone (Sample A) is not the mechanism of the salt activated method of the present invention. In other words, it is also necessary, following dispersion of the polymer in water, that the dry, positive heat of solution salt(s) be added to the polymer concentrates. While the application of artificial heat (rolling at 100°C) brings some response (250 cp Brookfield reading on Sample B, as compared to 180 cp Brookfield reading on Sample A), the effect is still no where the 1590 cp Brookfield reading used on the Control

30 Sample prepared by the salt activated method.

Claims

1. A method of preparing a liquid suspension of a hydrophilic polymer in an aqueous salt solution which comprises uniformly dispersing a hydrophilic polymer in water, and dissolving in the dispersion, an inorganic salt having a positive heat of solution, the salt being added in such an amount that

35 temperature in the dispersion is increased to at least 70°C.

2. A method as claimed in Claim 1 wherein the hydrophilic polymer is a carboxyalkyl cellulose ether, hydroxyalkyl cellulose ether, mixed cellulose ether, carboxyalkyl starch ether, hydroxyalkyl starch ether, mixed starch ether, polysaccharide gum, pregelatinized starch powder, stabilized partially dextrinized polysaccharide powder, toxic nonionic, or a mixture thereof.

40 3. A method as claimed in Claim 2 wherein the hydrophilic polymer comprises hydroxyethyl cellulose.

4. A method as claimed in any preceding claim wherein the inorganic salt is calcium chloride, calcium bromide, zinc chloride, zinc bromide or a mixture thereof.

45 5. A method as claimed in any preceding claim wherein the temperature generated by the heat of solution of the inorganic salt is at least 80°C.

6. A method as claimed in Claim 5 wherein the temperature generated by the heat of solution of the inorganic salt is at least 90°C.

7. A method as claimed in any preceding claim wherein the hydrophilic polymer is present in said suspension in an amount of from 0.25 to 30 g per litre.

50 8. A method as claimed in any preceding claim wherein the dispersion is mixed with an aqueous brine of predetermined density in an amount sufficient to produce a well servicing fluid of a predetermined density.

9. A method as claimed in Claim 8 wherein the aqueous brine contains at least one water soluble salt of an alkali metal, alkaline earth metal, Group Ib metal, Group IIb metal, or a mixture thereof.

55 10. A method as claimed in Claim 9 wherein the aqueous brine comprises calcium chloride, calcium bromide, zinc chloride, zinc bromide, or a mixture thereof.

11. A method as claimed in any of Claims 8 to 10 wherein the well servicing fluid has a density of from 1.39 to 2.30 g per ml.

60 12. A method as claimed in Claim 1 and substantially as hereinbefore described with reference to any of the Examples.

13. Liquid suspensions when prepared by a method as claimed in any of the preceding claims.